MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

Project ID: BAT028

Wenquan Lu (PI)

Joel Kirner, Linghong Zhang, Yan Qin, Steve Trask, Alison Dunlop, Bryant Polzin, and Andrew Jansen

Electrochemical Energy Storage
Chemical Sciences and Engineering Division
Argonne National Laboratory

2018 U.S. DEPARTMENT OF ENERGY VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING
WASHINGTON, D.C.
Jun 18th – 21st, 2018

OVERVIEW

Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2019

Barriers

- Development of EV batteries that meet or exceed DOE/USABC goals
  - Cost
  - Performance
- High energy active material identification and evaluation

Budget

- Total project funding in FY2016: $400K (as part of CAMP effort)
- 100% DOE

Partners and Collaborators

- The Cell Analysis, Modeling, and Prototyping (CAMP) Facility (Andrew Jansen, ANL)
- Materials Engineering Research Facility (MERF) (Gregory Krumdick, ANL)
- Post Test Facility (Ira Bloom, ANL)
- Industrial partners are listed at end

Argonne
NATIONAL LABORATORY

RELEVANCE

- An overwhelming number of materials are being marketed/reported to improve Lithium-ion batteries, which need to be validated for their impact on EV applications.

- CAMP Facility was established at ANL to provide a realistic and consistent evaluation of candidate materials. In order to utilize the facility more efficiently and economically, cell materials need to be validated internally to determine if they warrant further consideration.

- The benchmarking (validation) activities will not only benefit the CAMP Facility, but also provide an objective opinion to material developers. Moreover, the better understanding of the active materials at cell system level will speed up material development efforts.

Argonne
NATIONAL LABORATORY

OBJECTIVES

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the following criteria for EV applications.
  - Cycle life
  - Electrochemical performance
  - Abuse tolerance
  - Cost

- To enhance the understanding of advanced cell components on the electrochemical performance and safety of LIB.

- To support the CAMP Facility for prototyping cells and electrode library development.

APPROACH AND STRATEGY

- Collaborate with material developers and leverage ANL's expertise in electrode design and cell testing.

- Any cell material, which has impact on the cell performance, will be considered for testing, mainly in terms of

  – Electrochemical performance

  – Electrode optimization

  – Thermal stability

- The electrochemical performance will be validated using 2032 coin type cells under test protocol derived from USABC PHEV 40 requirements.

USABC Requirements of Energy Storage Systems for PHEV

USABC Requirements of Energy Storage Systems for PHEV			
Characteristics at EOL	Unit	PHEV-20 mile	PHEV-40 mile
Reference Equivalent Electric Range	miles	20	40
Peak Discharge Pulse Power (10 sec)	kW	37	38
Peak Regen Pulse Power (10 sec)	kW	25	25
Available Energy for CD (Charge-Depleting) Mode	kWh	5.8	11.6
Available Energy for CS (Charge-Sustaining) Mode	kWh	0.3	0.3
Maximum System Weight	kg	70	120
Maximum System Volume	L	47	80

Test Protocol development

➢ In order to conduct the electrochemical characterization of the battery chemistries for Applied Battery Research for Transportation (ABR) program, C rate and pulse current was calculated for coin cells according to PHEV 40 requirements.

Argonne
NATIONAL LABORATORY

TECHNICAL ACCOMPLISHMENTS AND MILESTONES

- Electrochemical characterization of nickel rich high energy cathode materials were completed.
  - $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811, Targray)
  - Concentration gradient NMC811-CG (MERF)

- Electrochemical characterization of anode materials.
  - Silicon based high energy anodes
  - Graphite with high rate performance

- Other cell components, such as chemical pre-lithiation agents, conductive additives, separators, binders, etc., have also been investigated.

Argonne

HIGH ENERGY CATHODE MATERIALS (NMC)

- Nickel rich $LiNi_xMn_yCo_zO_2$ (NMC) is gaining momentum as high energy cathode materials for electric vehicle applications. Following NMC532, NMC622 is penetrating the market, and NMC811 is expected to be next generation high energy cathode material. However, the higher energy density of nickel rich NMC comes at the expense of lower thermal stability.

- The MERF at ANL is working on core-gradient concepts to coat the nickel-rich core with low nickel NMC to improve the thermal stability.
  - Core-gradient NMC811 has fixed nickel rich composition for the core, but concentration gradient for its shell, which is a hybrid of core-shell and concentration-gradient.
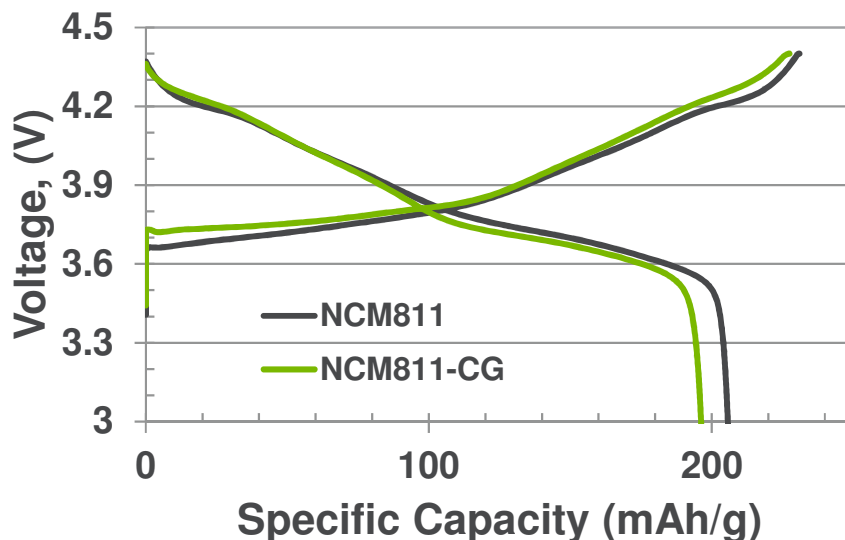
NMC811-CG has been synthesized by MERF and is being tested by the CAMP Facility in pouch cells (BAT167 and BAT030)

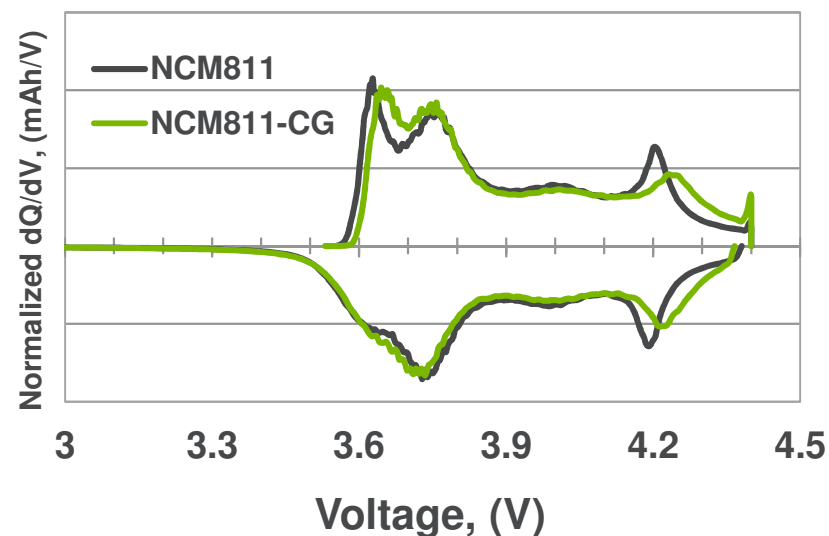**811 Core-Gradient**

Core NMC955   Surface NMC333

Ni
Mn
Co
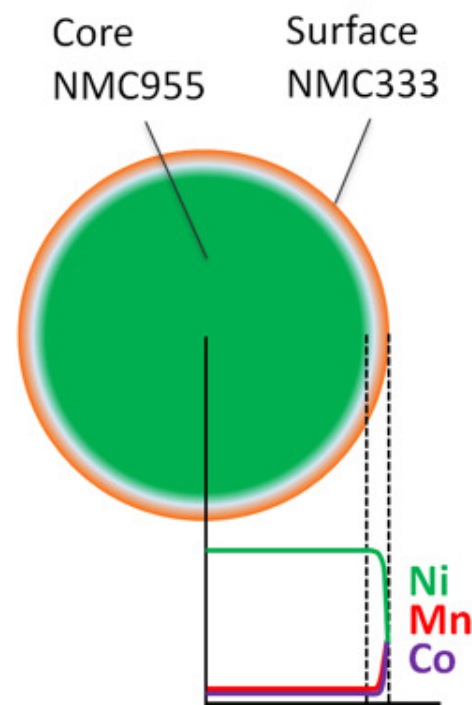
HALF CELL CHARACTERIZATION OF NMC811-CG

First cycle voltage profile overlay

3rd cycle dQ/dV overlay

Voltage window: 3.0V to 4.3V
C/10 rate for 3 formation cycles
1st formation specific capacity (mAh/g)

	Delith. Cap	Lith. Cap.	CE (%)
NCM811 (Targray)	233 ± 3	208 ± 2	89.44
NCM811-CG	227 ± 1	198 ± 1	87.39

- Very similar electrochemical performance was observed for both NMC811.

- Slight voltage peak shift suggests a local chemistry effect on the electrochemistry of NMC811.

Argonne

8

FULL CELL CHARACTERIZATION OF NMC811-CG

- In order to obtain the electrochemical performance of NMC811-CG, coin-type full-cells were adopted to address the concern of lithium metal in half-cells.

- The commercial NMC811 was used as control. Graphite was used as the anode.

- The N/P* ratio was carefully matched, which is very critical for performance evaluation.

Voltage window: 3.0V to 4.3V
3rd Cycle, Specific Cap (mAh/g)

	Charge	Discharge	CE (%)
NCM811 (Targray)	174 ± 3	173 ± 4	99.56
NCM811-CG	185.0 ± 10.5	184.6 ± 9.6	99.78

(error bars are ± 1σ, n = 3)

* N/P ratio is the area specific capacity ratio of negative and positive electrode.

Cathode Compositions (14 mm):

	NCM811 (Targray)	NCM811-CG MERF
Active	90%	90%
C45	5%	5%
Binder (PVDF)	5%	5%
Laminate Mass	14.5 mg/cm²	~18.1 mg/cm²
Laminate Thickness	34 μm	45 μm
Porosity	~34%	~30%
Areal Capacity	1.92 mAh/cm²	2.63 mAh/cm²

Anode Compositions (15 mm):

	Graphite, A12	Graphite, MagE
Active	92%	92%
C45	2%	2%
Binder (PVDF)	6%	6%
Laminate Mass	6.07 mg/cm²	9.15 mg/cm²
Laminate Thickness	43 μm	65 μm
Porosity	~34.9%	~35.1%
Electrolyte (flooded)	Gen2	Gen2
Areal Capacity	2.25 mAh/cm²	3.32 mAh/cm²
N:P ratio	1.17	1.26

Argonne
NATIONAL LABORATORY

# FULL CELL CYCLING OF NMC811-CG
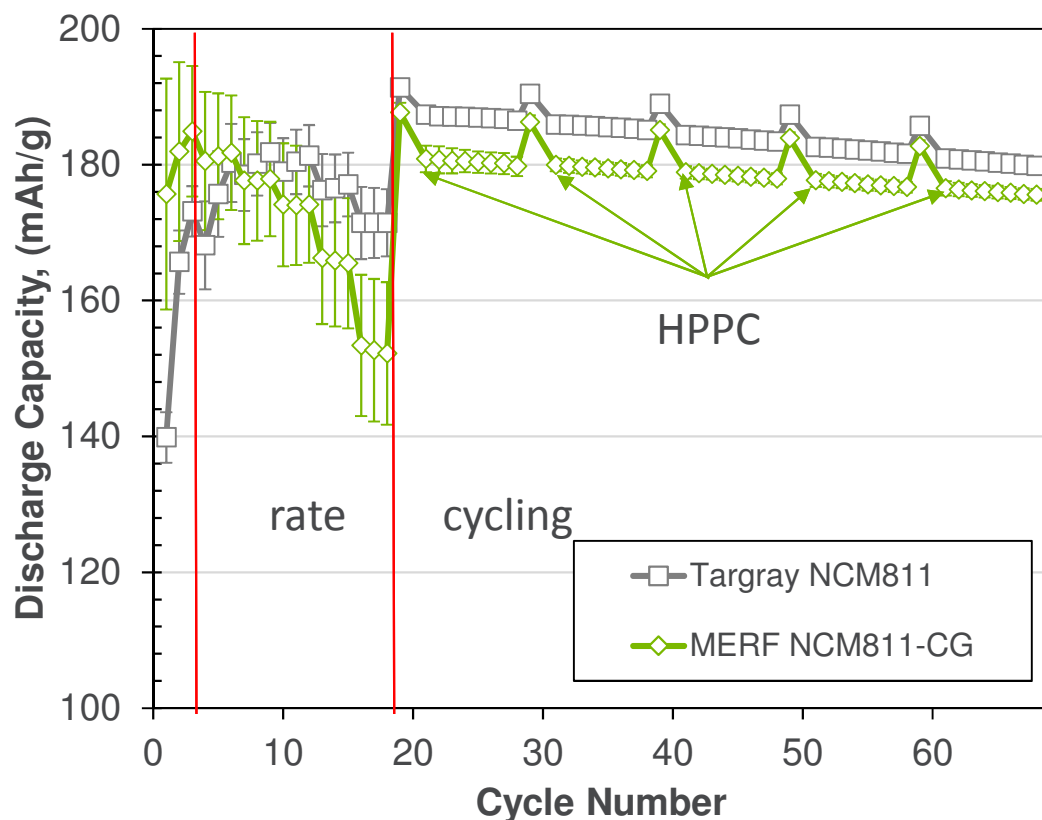
Electrochemical testing (3.0V to 4.3V):

1. Formation: 3 cycles of C/10
2. Rate: charge: C/5, discharge: C/5, C/3, C/2, 1C, 2C
3. Cycling: 1 cycle of C/10, 1 cycle of HPPC, and 8 cycles of C/3
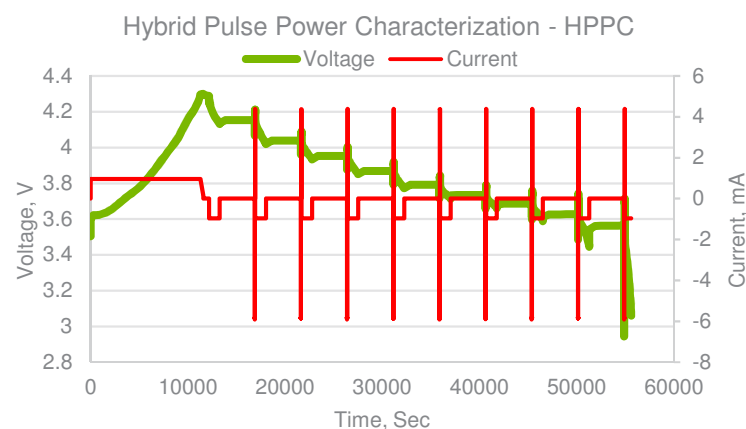
- Consistent to lithium half cell results, the full cell capacity of normalized to NMC811-CG is less than that of commercial NMC811.

- The cycling performance of NMC811-CG is similar to that of commercial NMC811.

# HYBRID PULSE POWER CHARACTERIZATION OF GRAPHITE/NMC811-CG FULL CELL
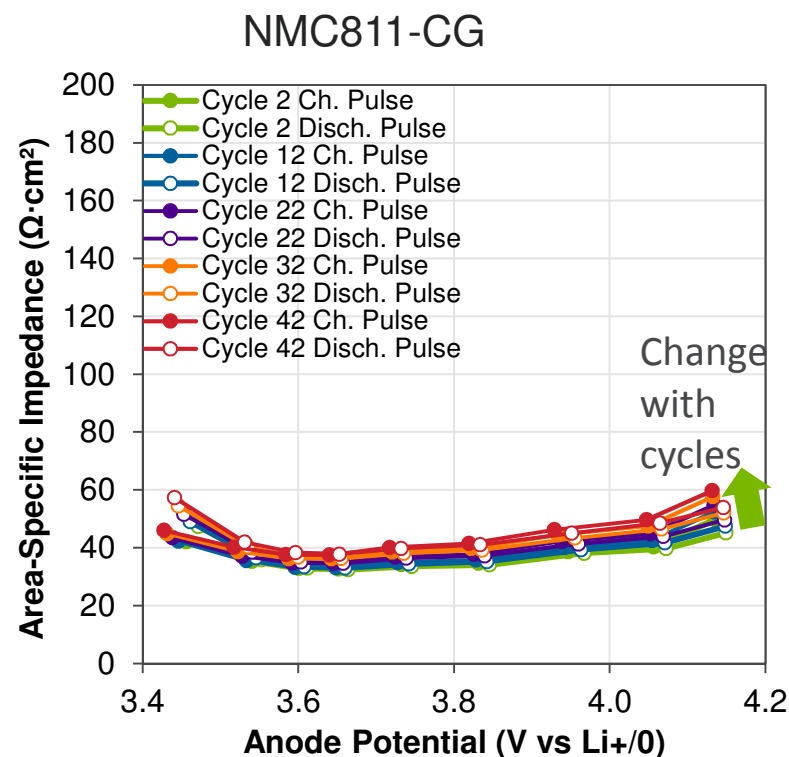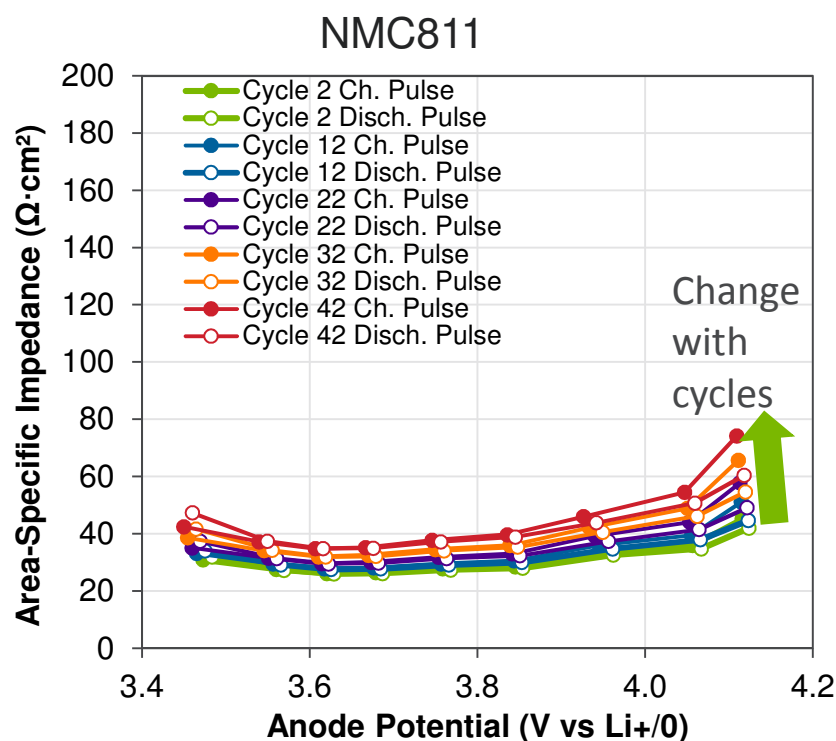
Cycle # in plot is the cycle number during the cycling test.

- Area specific impedance (ASI) of commercial NMC811 increases more than that of NMC811-CG with cycling.

- See BAT030 and BAT167 for pouch cell testing

SILICON ELECTRODE

SEM of commercial SiO

- Silicon monoxide (SiO) has been investigated as the next-generation anode material for lithium-ion batteries due to its high energy density. Compared to commercially used graphite, SiO has a theoretical gravimetric capacity of 1710 mAh/g and volumetric capacity of 1547 Ah/L and can offer an 18% increase in volumetric energy density on the cell stack level.

- SiO is composed of Si nano-domains in a SiO_2 matrix.
  - Mitigate the volume change during cycling and better cycling stability
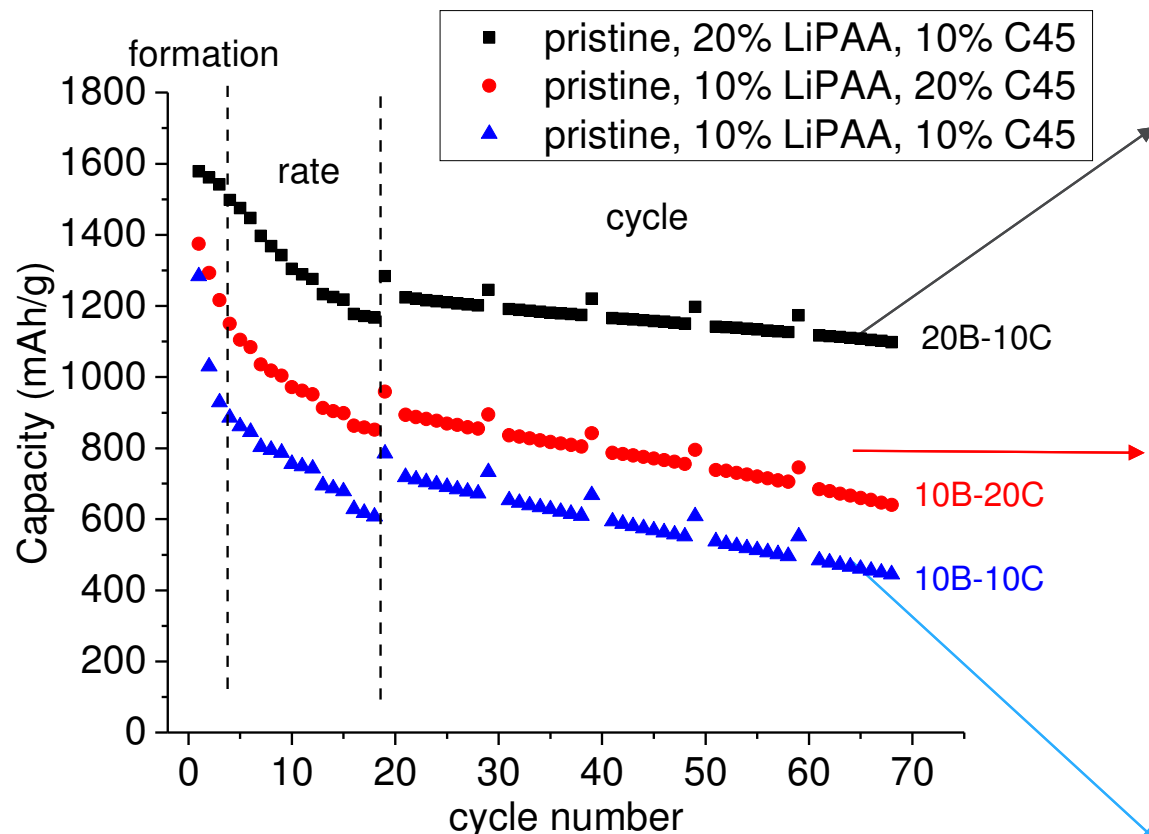 - less solid-electrolyte interphase (SEI) formation.

5 μm
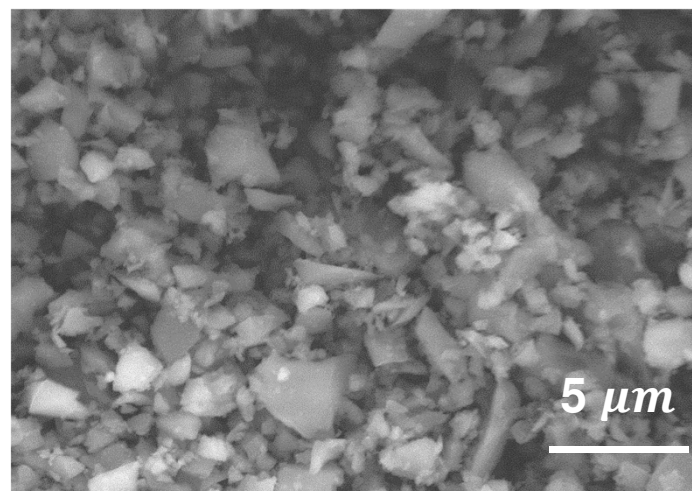
Micron particle size for easy handing.
Si domain from TEM

5 nm

Argonne
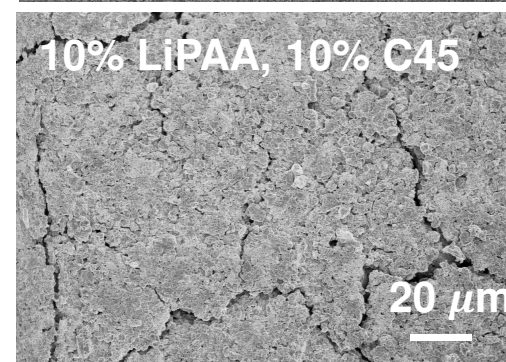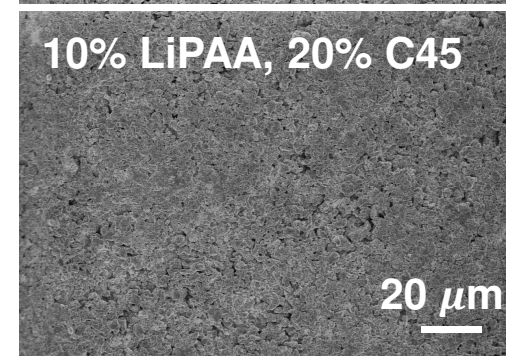NATIONAL LABORATORY

12
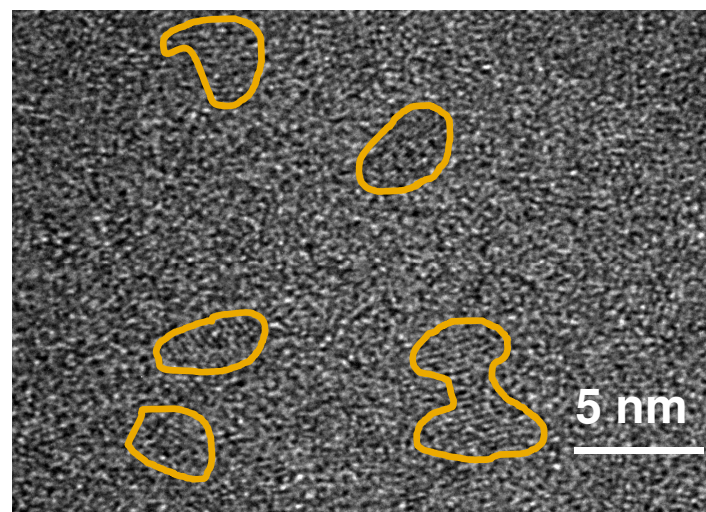
SiO ELECTRODE COMPOSITION OPTIMIZATION

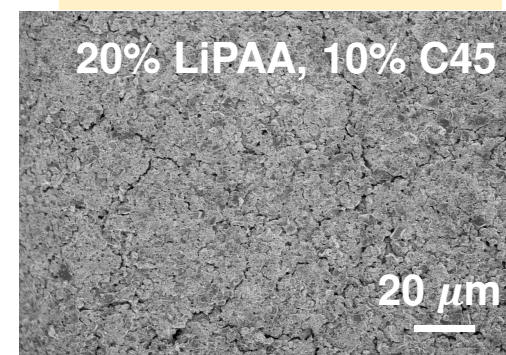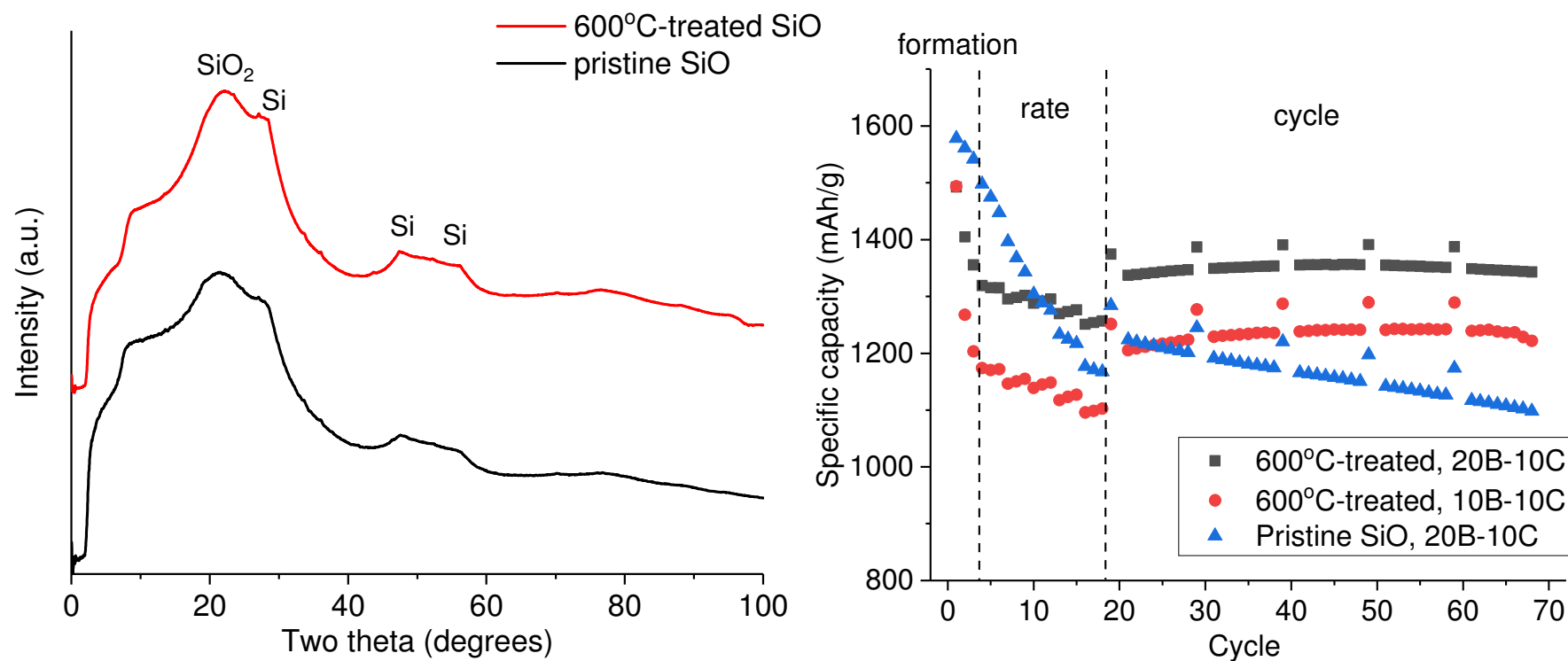Cycled SiO electrode

- Significant improvement in capacity retention was observed when the electrode composition is optimized.

- SEM images of cycled SiO electrode suggested that the optimized electrode composition can improve the electrode integrity.
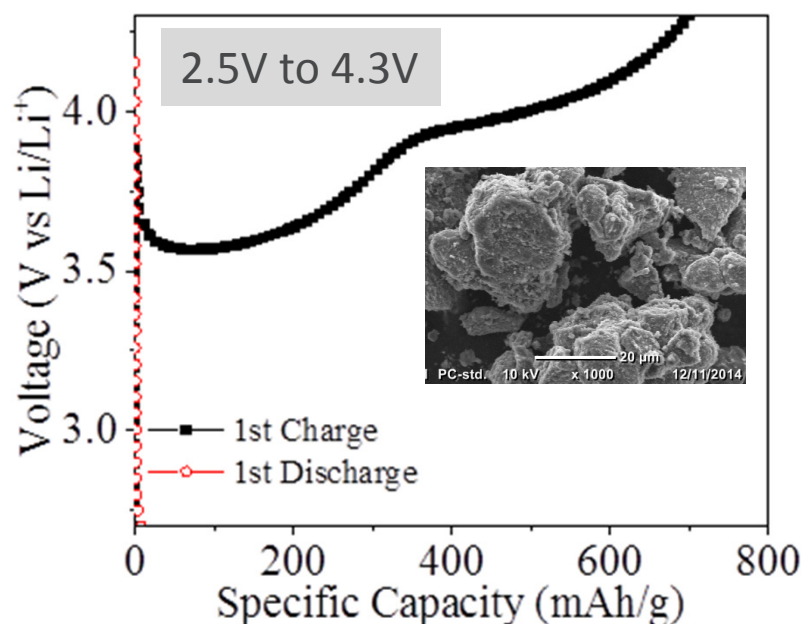
Argonne
NATIONAL LABORATORY

13

ANNEALING EFFECT ON SiO

- According to the XRD patterns, annealing SiO in the argon atmosphere results in the slight increase of Si domain size from 3.36 nm to 3.54 nm

- Significant improvement in capacity retention as well as less dependency on the electrode composition was observed for annealed SiO, suggesting improvement of the intrinsic stability of the SiO particles
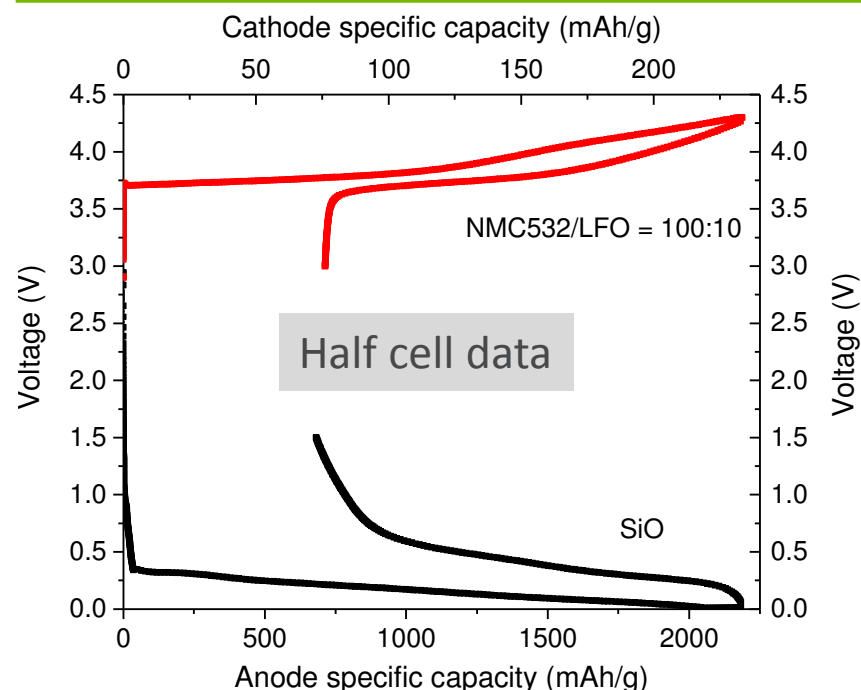
Argonne
NATIONAL LABORATORY

SIO/NMC532 FULL CELL WITH LITHIUM INVENTORY

LFO is currently in the hands of the CAMP Facility for prototyping: See BAT030

Li_5FeO_4 powder

2.5V to 4.3V


- Li_5FeO_4 was developed at ANL with high lithium content:
  - 700mAh/g was achieved during delithiation.
  - No discharge capacity within normal operation voltage window.

- The annealed SiO is paired with an NCM-LFO cathode, where LFO (Li_5FeO_4) is used as a prelithiation reagent to compensate the 1st cycle irreversible capacity loss of SiO electrode.

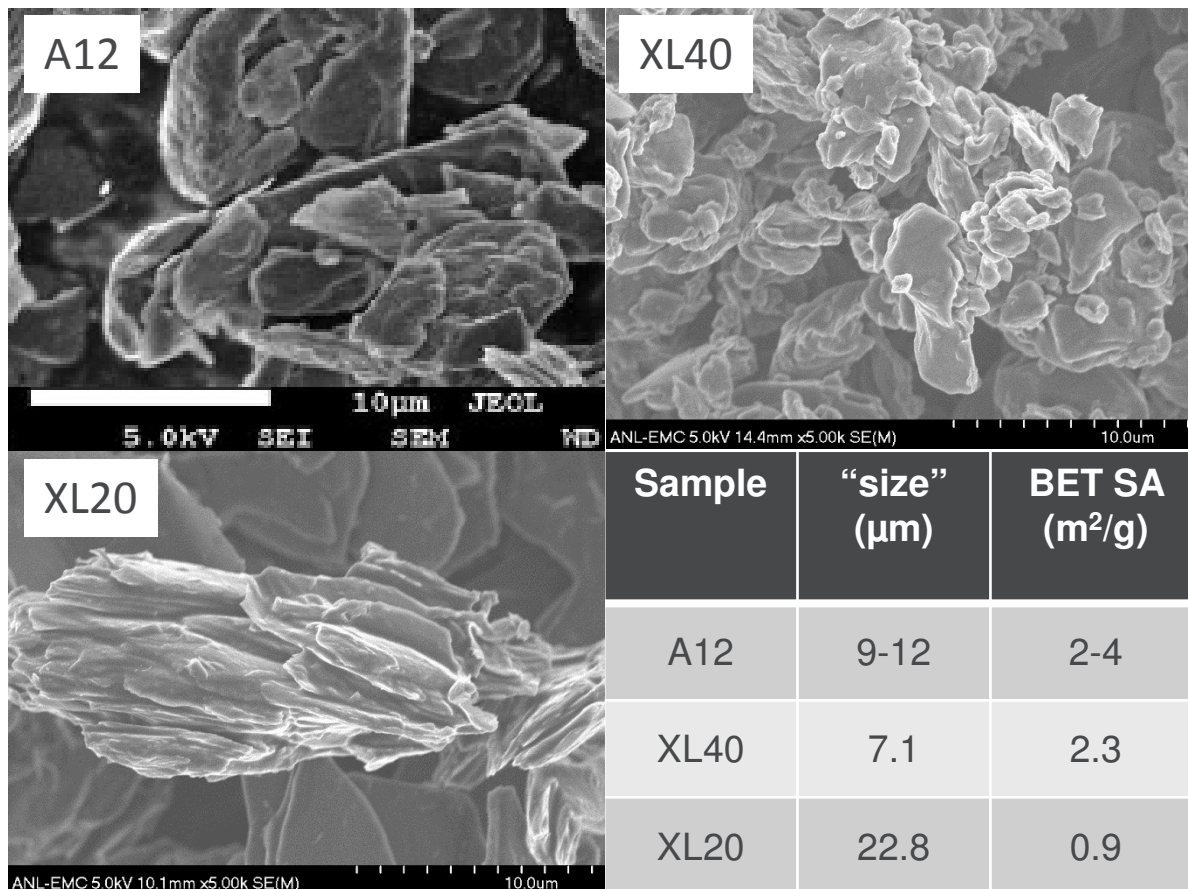# CYCLE PERFORMANCE OF SiO/NMC532-LFO FULL CELL
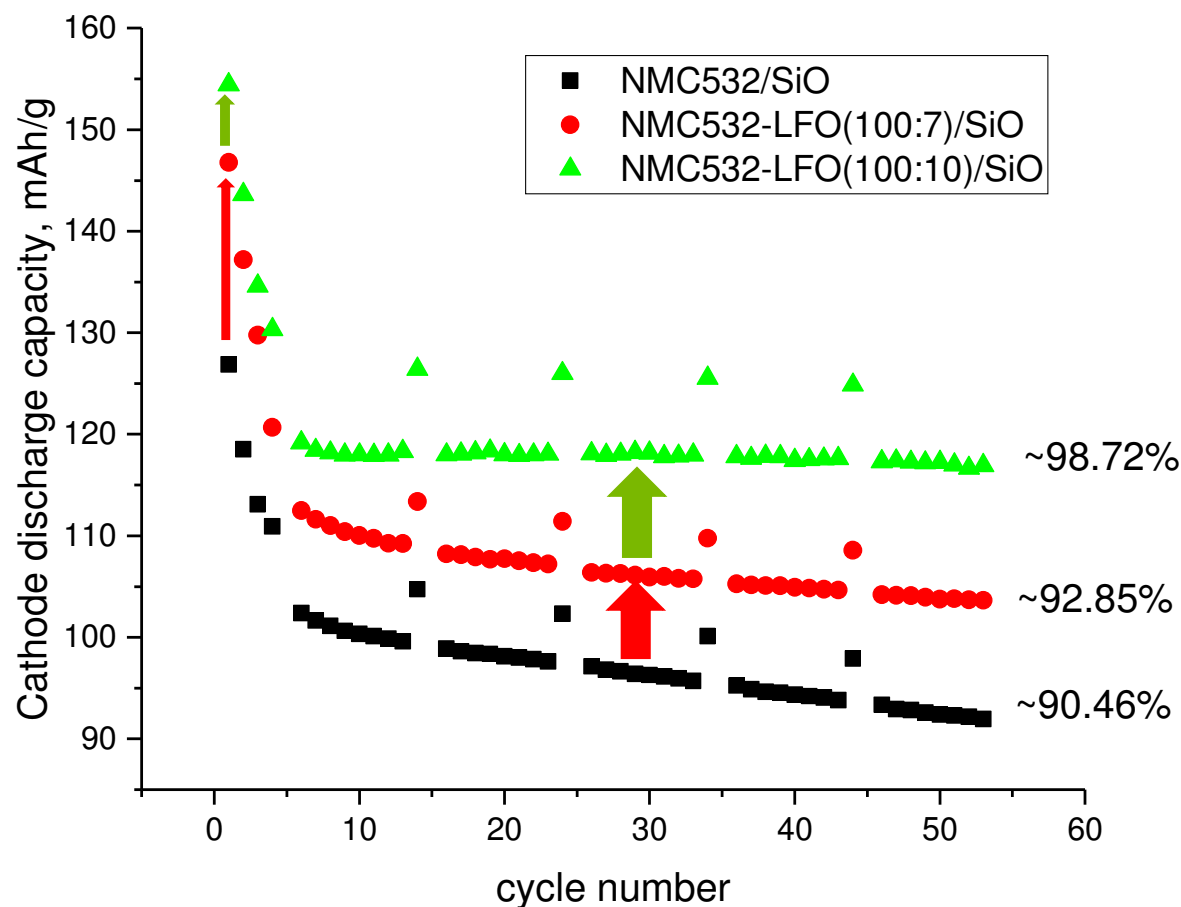
- Adding 7% of LFO can increase the usable capacity of NMC532 cathode.

- In addition, the capacity retention of SiO/NMC532-LFO full cell is also improved with prelithiation.

- Addition of more LFO (10%) leads to better capacity retention by avoiding cycling SiO at the less stable voltage ranges of NMC

SYNTHETIC GRAPHITE AS ANODE

- Natural graphite is the current dominant anode material due to its high energy density and low cost.

- Though expensive compared to natural graphite, synthetic graphite is worthy of investigation for LIBs due to its higher purity and different properties.

- Two synthetic graphite materials were obtained and tested in coin type full cell using natural graphite A12 as a control.

Sample	"size" (µm)	BET SA (m²/g)
A12	9-12	2-4
XL40	7.1	2.3
XL20	22.8	0.9

FULL CELL INFORMATION

- Graphite/NMC532 coin-type full cells were used to characterize the rate and cycle performance of synthetic graphite samples.

- Full cells were cycled between 3.0V and 4.2V. The electrode balancing information is shown in Figure below.

Half cell data

Voltage (V vs Li$^{+/0}$) vs Areal Capacity (mAh/cm^2)

- CAMP A-C015A
- XL20
- LCV
- UCV

4.2 V UCV

Expected Cap:
1.36 mAh/cm²
2.09 mAh/cell
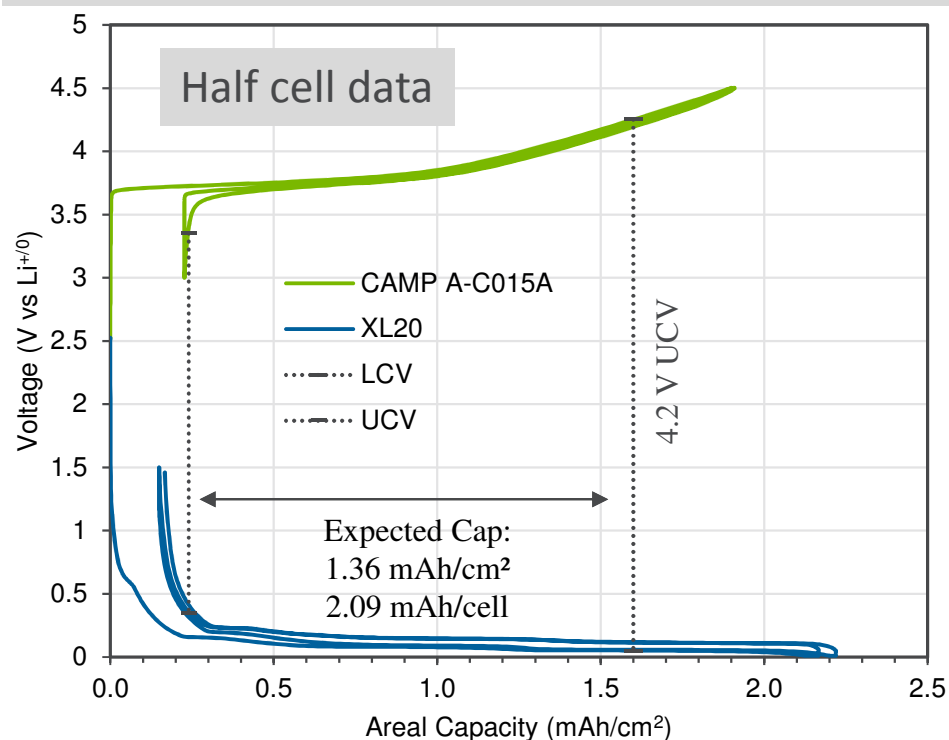
Electrode properties

Anode Composition (Graphite):
- 92 wt% active, 2% carbon black (Timcal C45), 6% PVDF
- ~6 mg/cm² laminate; ~34 μm laminate thickness;

Cathode Composition (LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$, "NMC532", C015A CAMP @ANL):
- 90 wt% active, 5% C45, 5% PVDF
- ~9.12 mg/cm² laminate, 34 μm laminate thickness

Sample	1st Cycle Cap. (CE)	3rd Cycle Cap. (CE)
A12	348 ± 10 mAh/g (91.1%)	364 ± 1 mAh/g (99.2%)
XL40	319 ± 4 mAh/g (91.0%)	327 ± 1 mAh/g (99.3%)
XL20	345 ± 3 mAh/g (93.3%)	351 ± 1 mAh/g (99.5%)

Argonne
NATIONAL LABORATORY

RATE PERFORMANCE OF GR/NCM FULL CELL
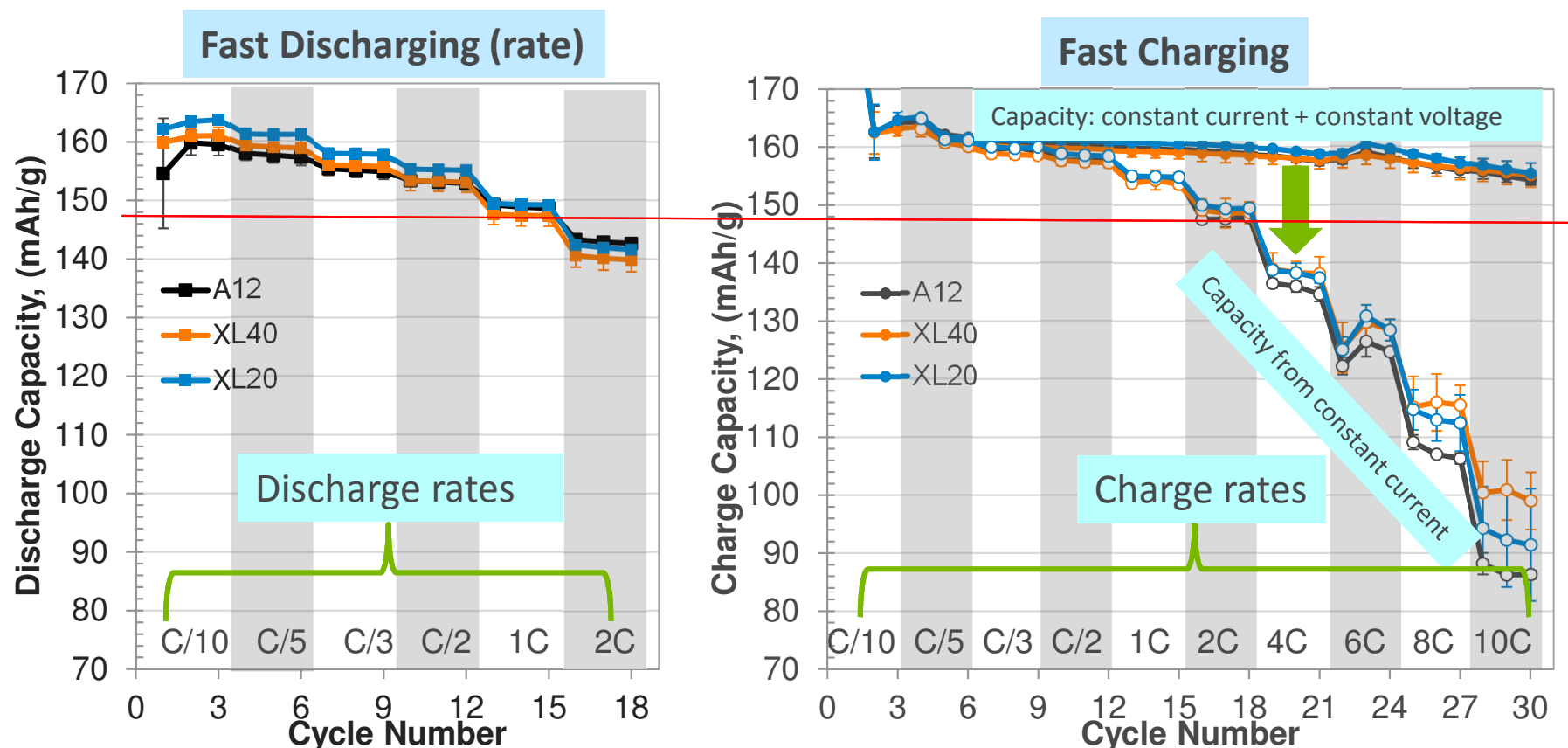
- A12 has better rate performance, while XL20 and XL40 have better fast charging performance.

- More than 88% capacity was obtained for XL20 with 4C charging rate

- The full cells show better charging capability: 1C discharge capacity is less than 1C charging capacity

19

Argonne
NATIONAL LABORATORY
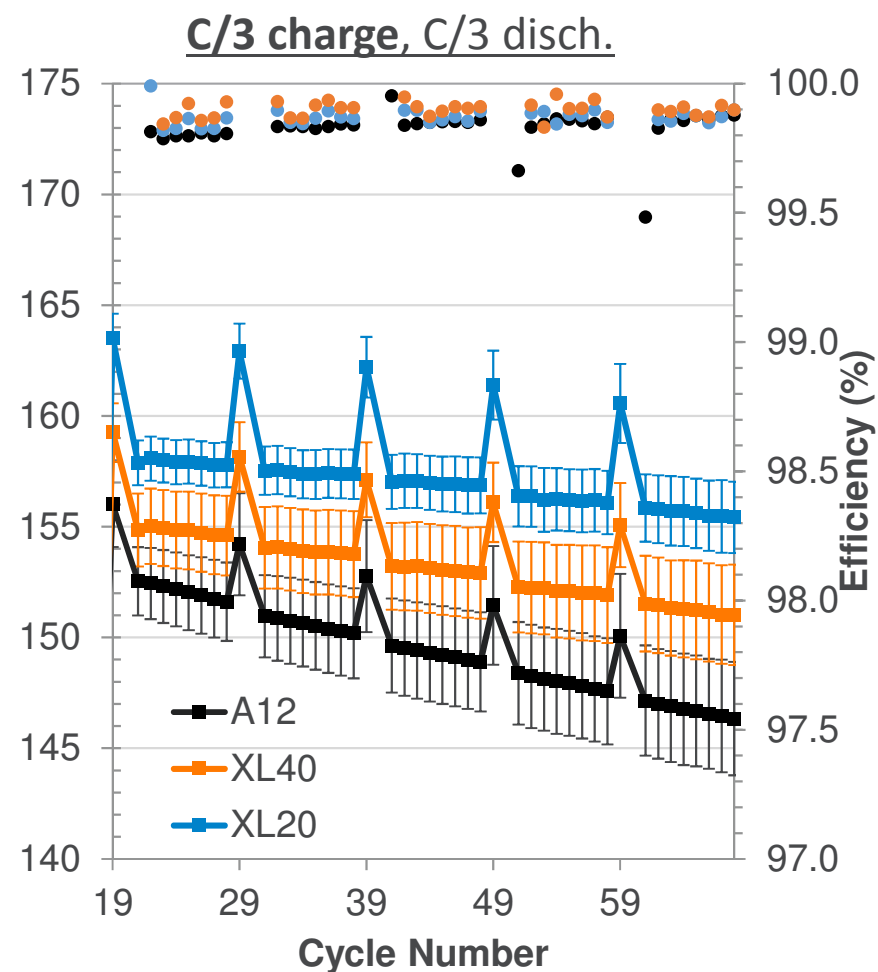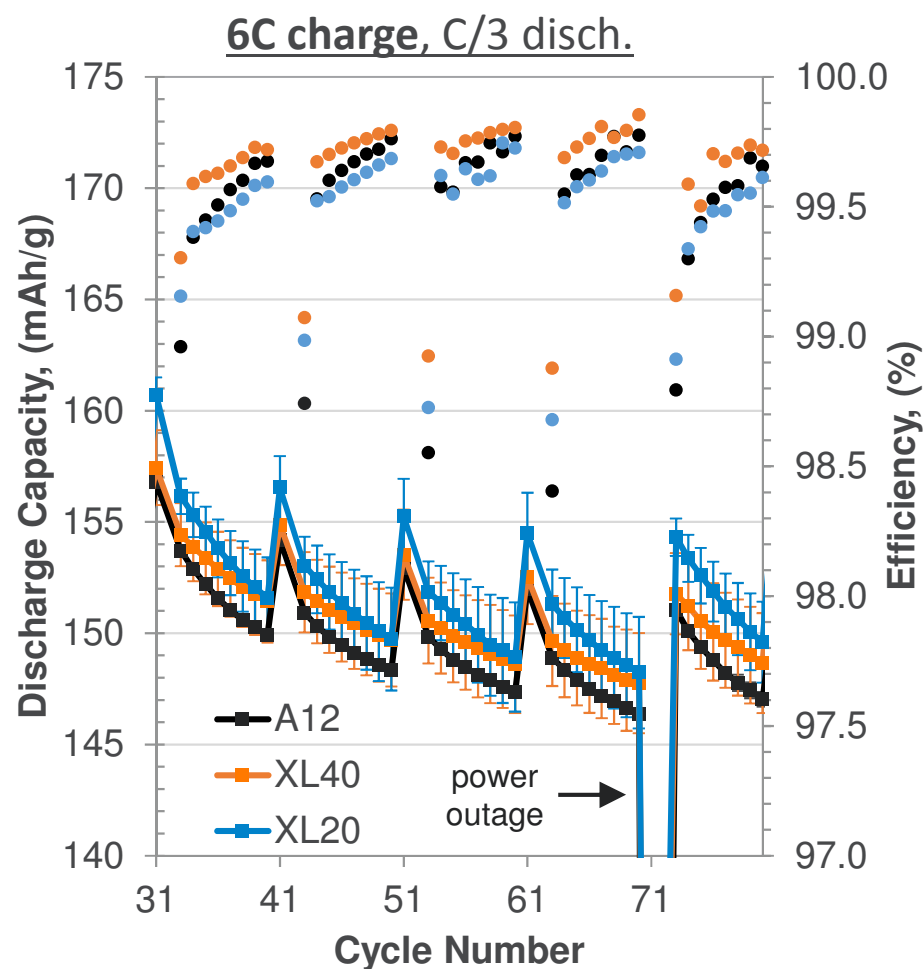
CYCLE PERFORMANCE

- Full cells using XL20 and XL40 graphite show better cycling performance with 6C rate charge.

Argonne
NATIONAL LABORATORY

POST MORTEM ANALYSIS
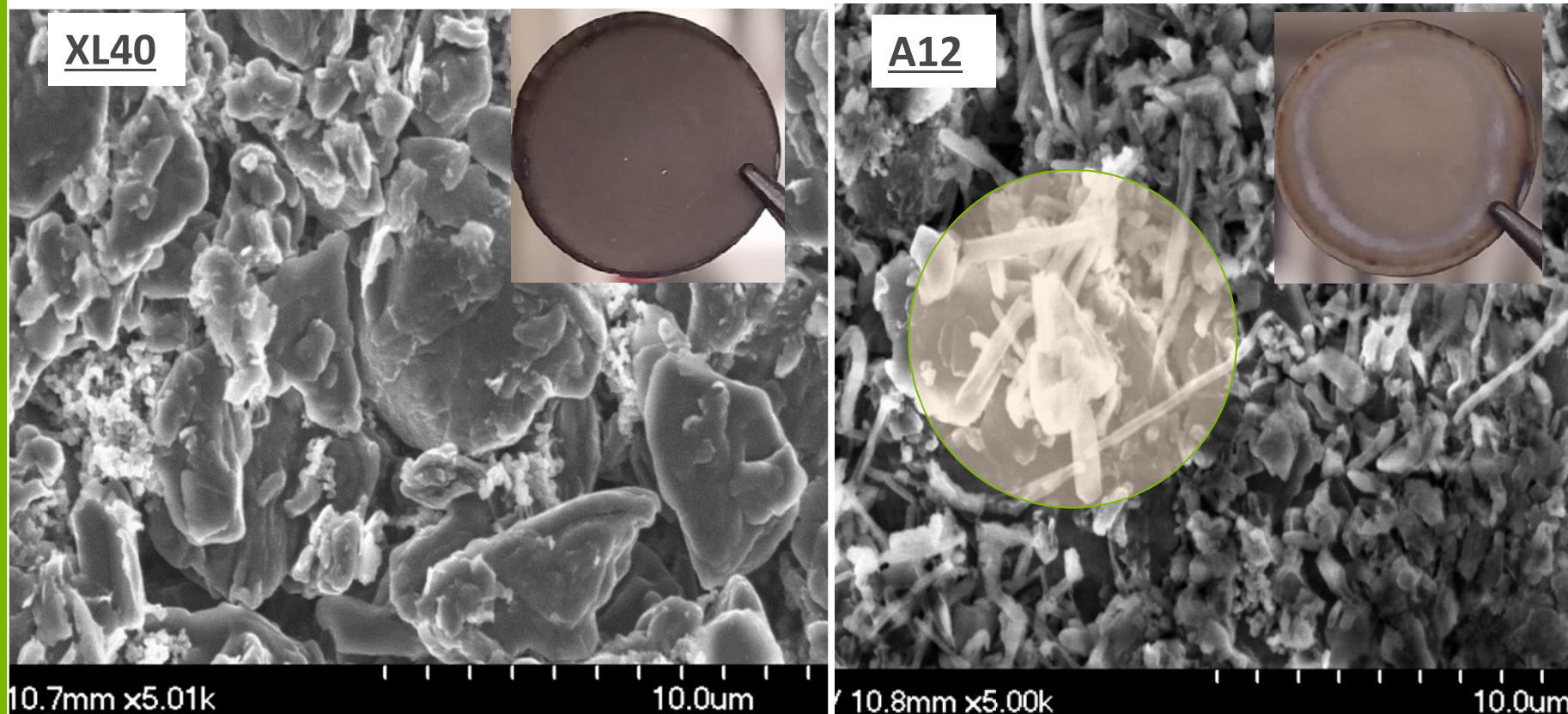
- Lithium dendrite (in circle) was observed for the cycled A12 electrode after cycling with 6C charge rate, but not seen on the cycled XL40 electrode, which is consistent to the cycling performance.

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

Comments: Most reviewers agreed that this project is relevant to DOE objectives to support the early stage EV research and development. A concern on the coin-type cell approach was raised multi times by the reviewers for this materials benchmarking activity. My response is below.

Response: The materials benchmarking activity is part of Cell Analysis, Modeling, and Prototyping (CAMP) Facility. Under this project, the promising battery materials, especially active materials, will be mainly electrochemically characterized. The learned knowledge will be handed over to the CAMP Facility for further investigation using commercial grade large format cells (pouch/18650 cell) to get more realistic and comprehensive information.

Furthermore, the CAMP facility works closely with the Post Test Facility (PTF) when in-depth analysis is needed to better understand the cell performance and related failure mechanism.

Argonne
NATIONAL LABORATORY

COLLABORATION

- The partners and collaborators include
  - National labs: ANL, BNL, ORNL
  - Universities: IUPUI
  - Industries: Alabama Graphite, BTR, Cabot, Celgard, HuaWei, Hydro Quebec, JSR, Navitas, Osaka Titanium Corp., OSiAIC, Paraclete Energy, Physical Science Inc., PPG, Silican, SiNode, Superior Graphite Co., Targray, Toda Kogyo
- The CAMP Facility is open to work with industries to advance the LIB technologies for EV application.

REMAINING CHALLENGES AND BARRIERS

- High energy active material identification and acquisition remain a challenge.
  - Existing commercial active materials can't meet or exceed DOE/USABC the goals.
  - Getting access to advanced active materials is not always successful.
  - The barrier becomes even larger when the test results have to be made to the public.

- As a benchmarking activity, the focus of this work is to simply validate the performance of cell materials (including electrochemical and thermal properties).
  - However, necessary understanding is inevitable.
  - A good balance between the validation and research needs to be fine-tuned.

Argonne △
NATIONAL LABORATORY

FUTURE PLAN

- The focus will be high energy anode/cathode materials,
  - Silicon and other metal alloys, including new binders, electrolytes/additives, and advanced conductive additives to address the volume expansion and mitigate the parasitic reactions.
  - Prelithiation may be very critical for Si electrode development. We will expand the research effort on prelithiation.
- Continue to work closely with research institutions and industrial suppliers to enable the LIB technology for EV applications.
  - Promote the collaboration with the domestic material suppliers

Argonne
NATIONAL LABORATORY

SUMMARY

- Concentration gradient NMC811 from MERF was tested using graphite/NCM811 full cells. Comparable electrochemical performance, but less impedance rise during cycling test was obtained comparing to commercial NMC811.

- Silicon electrode (SiO) was explored as high capacity anode.
  - Electrode optimization was found to be critical for its performance.
  - The heat treatment of SiO particles was also found to have beneficial effect on the silicon electrode.
  - Lithium inventory agent (Li_5FeO_4) was used to compensate the 1st cycle capacity loss of SiO and better cycling performance was obtained in SiO/NMC532-LFO full cell.

- Synthetic graphite as an anode replacement for natural graphite was investigated, which was found to have better charging performance.

Argonne
NATIONAL LABORATORY

CONTRIBUTORS AND ACKNOWLEDGMENTS

ANL

- Abraham, Daniel
- Bareno, Javier
- Bloom, Ira
- Dees, Dennis
- Dose, Wesley
- Johnson, Christopher
- Krumdick, Gregory
- Liu, Qi
- Liu, Yuzi

- Loizzo, Hannah
- Maroni, Victor
- Ren, Yang
- Shin, Youngho
- Xiao, Xianghui
- Vaughey, Jack
- Wu, Yimin
- Yang, Zhenzhen
- Zhang, Lu

Facilities

- Advanced Photon Sources
- Center for Nanoscale Materials
- Material Engineering Research Facility (MERF)
- Post Test Facility (PTF)

Argonne ▲
NATIONAL LABORATORY